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the flat fiber surfaces. The pressure on the area of overlap is, to a first approximation, the quotient of the surface tension divided by the radius of the meniscus. As evaporation proceeds, the water film does not draw in from the edges of the overlapped area, but rather draws the flat surfaces together with an ever-increasing pressure. By the time the flat surfaces are 1 μm apart, the pressure is calculated to be 145 kPa [21 psi]; at 10 Å apart, it is 145,000 kPa [21,000 psi]. Making the same estimation for round fibers, Campbell[15,16] has calculated that if the diameter of two round fibers is 30 μm, and they are lying parallel with a common water contact in the nip between them, the pressure pulling them together will be nearly 620 kPa [90 psi]. In the case of the smaller fibrils with a diameter of 2 μm, the pressure would be 3700 kPa [540 psi]. The forces of surface tension act in a direction normal to the surface of the sheet resulting in a several-fold reduction in thickness, compared with only a small change in area.[17]

Surface tension is so important in fiber bonding that the presence, either from poor washing or deliberate addition, of even small amounts of agents that reduce the surface tension will result in a sheet of low density. This lower density is probably the result of the reduction of contracting forces due to reduced surface tension; however, it may also be the result of the prevention of hydrogen bonding resulting from the adsorption of surfactant which masks the polar grouping on the surface of the fibers.[13] Removal of the interfiber water by sublimation at -6°C so that surface tension forces are no longer a factor results in a highly porous, bulky sheet of high opacity and low strength due to a reduction in fiber bonding.[18]

Lyne and Gallay[17] proved that the strength at very low solids content was due almost entirely to the effect of surface tension by making sheets of glass fibers, which are nonbonding. Just as with cellulose fibers, the glass fibers were pulled together in the thickness direction of the web, as water is removed, with a remarkable increase in density and a correspondingly sharp increase in tensile strength. At about 25 percent solids, the web of glass fibers reached a maximum tensile strength, and further removal of water caused the tensile strength to decrease to a very low value. Unbeaten spruce sulfite sheets showed a plateau in the development of tensile strength with increasing solids at about 25 percent solids, suggesting that surface tension was dominant up to that level, while interfiber bonding was developing above 25 percent solids.[19]

Stages in Fiber Bonding During Dewatering of Wet Webs

Several stages in fiber bonding take place during the dewatering of wet webs. As mentioned above, surface tension is the principal factor in sheet consolidation in the early stages of drying up to a solids content of about 20 to 25 percent.[19] During this period there is a rapid decrease in the caliper of the wet web as water is removed, with increasing air intrusion into the web of fiber and water. As shown in Figure 7-1[17], the wet-web tensile strength is increasing very rapidly up to 25 percent solids although the tensile strength achieved is still low. The plateau due to reaching the maximum effect of surface tension is clearly seen, in the range of 25 to 45 percent solids depending upon the type of pulp.
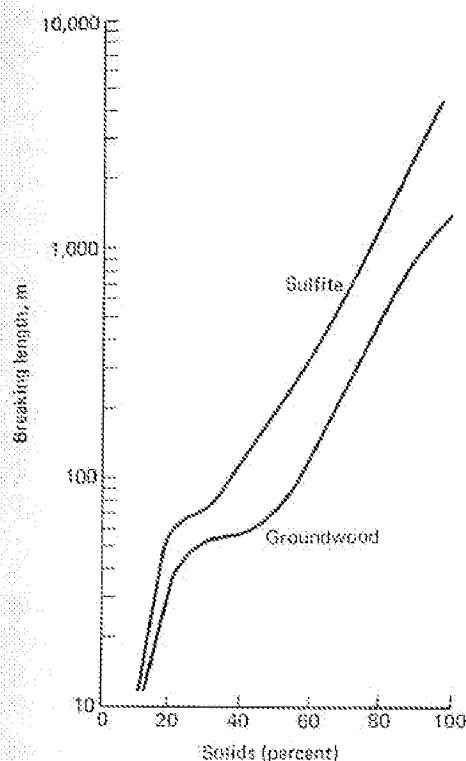
Figure 7-1. Effect of solids content on sheet strength.

In the low-solids area where surface tension supplies the pressure holding the fibers together, the resistance to tensile pull is likely to be frictional. In a simpler case, dry glass-fiber webs probably owe their low but very appreciable strength entirely to friction.[17] Pulp fibers, with a relatively low modulus and high degree of plasticity when wet, should show even greater frictional resistance than glass fibers for the same surface area involved. The much higher tensile strength of webs of beaten spruce fibers in the region of 25 percent solids, compared with glass fibers, is consistent with the concept of greater friction. Also, the elongation is strikingly high, reaching as much as 25 percent of the original length, as might be expected of long fibers held together by surface tension, but unbonded and therefore free to slide past each other lengthwise, inhibited only by friction.

The completely wet paper web, just after being formed, contains water between fibers and inside of fibers. The effect of surface tension discussed above is manifested when the water between fibers has been partially displaced and air intrusion occurs. When the interfiber water is nearly or completely displaced by air, as the result of drainage or drying, true interfiber bonding begins. Robertson[20] considers the water inside of the fibers to be represented by the measurable hydrodynamic volume of the fibers, and to be a summation of the swollen volume of the cellulose, lignin, and hemicelluloses forming the fiber wall, plus water occluded in the lumen, pits, and other voids, plus water immobilized by fibrillar or lamellar elements on the fiber surface plus the volume of any swollen or unswollen material adsorbed on the fiber surface. Brecht[21] considers all of this to be water of swelling. It is closely

related to the water measured in the determination of "water-retention value." It is this volume of water, however described, which is increased by beating. The beginning of the loss of this water is the point at which fiber bonding begins. Fiber bonding continues to develop as further water is lost. Interfiber bonding develops because the fiber elements are in close contact, compacted by the forces of surface tension, allowing true bonding, probably hydrogen bonding, to occur when the film of water between the fibers disappears. Intrafiber bonding also occurs as the water is lost internally, for example, between the annular lamellae which make up the fiber walls, as described by Stone and Scallan.[22] The presence of the point of inflection in the curve of tensile strength versus percent solids, when the solids is as low as 25 percent, leads to the conclusion that the loss of interfiber water precedes the loss of intrafiber water.

Loss of water inside of the fiber and development of intrafiber bonding are accompanied by a shrinkage, small in the longitudinal direction of the fiber and large in the transverse direction of the fiber. Where two fibers cross each other and are in close contact, shrinkage must now occur in both directions in both fibers if the areas in contact are to remain bonded, as drying proceeds. Page[23] postulates that this transverse shrinkage of the bonded crossed fibers gives rise to kinks and microcompressions throughout the structure in the immediate area of the bond, to a degree controlled by drying restraints. As a result, in an open, poorly bonded sheet, the shrinkage of the web reflects mostly the shrinkage in the longitudinal direction of the fibers and is small, while in a well-bonded sheet the transverse shrinkage of the fibers predominates and the shrinkage of the web is large. It has been recognized that fiber bonding and web shrinkage are quantitatively related. Byrd[28] has used the web-shrinkage energy as an index of network fiber bonding.

Types of Bonds in Dried Paper

When paper is formed in water and dried, it is strong. When the paper is soaked in water again it disintegrates. It is as though the fiber surfaces were glued together with a water-soluble glue in that the adhesion occurs when the water evaporates but is lost when the bond is rewetted. The "glue" in the paper fiber bond does not wash off, because the paper disintegrated in water can be reformed and dried, and will again be strong. Thus, there is no "glue" as a separate entity, but rather the fiber surface in and of itself has the adhesive ability. The adhesive ability of the fibers can be demonstrated without making paper. If two wet fibers of a papermaking wood pulp are pressed together and dried, they will be firmly bonded.[25,26] Papermaking wood fibers will, similarly, form bonds when pressed wet against never-dried cellophane.[27] Both of these methods are important means of determining interfiber bond strength.

Such evidence for the specific adhesiveness of cellulose for cellulose, brought about by water, focuses attention on chemical effects. The mechanical effect of friction has already been seen to provide only a low level of strength, when surface tension is the compacting force. The mechanical effect of fiber interlocking and crimping might under certain circumstances provide strength to a paper web, but

in general the strength of papers which are other than bone dry does not seem to have an important mechanical component. The effect of the moisture content of cellulose in equilibrium with ordinary atmospheres in plasticizing and flexibilizing the cellulose is a factor in preventing mechanical interlocking. Molecular chemical interactions may be: primary valence bonds, polar bond attractions, hydrogen bonds, or van der Waals' that is, nonpolar, nonionic attractions.

Primary valence bonds seem to be of negligible occurrence in the bonding which takes place when paper is made from cellulose fibers. Paper is not as strong as plastic films, which are crosslinked by primary valence bonds. In quantitative terms, primary valence bonds require about 30 kcal/mole for disruption compared with about 5 kcal/mole for strong hydrogen bonds, and about 2 kcal/mole for other polar bonds. The bonds in paper seem to be of a strength consistent with the strength of polar bonds in general and the hydrogen bond in particular. The easy appearance and disappearance (in water) of the bonding in paper are not like the reactions of chemical functional groups forming primary valence bonds, none of which are known to be so easy both to induce and to reverse. The origin of the realization that hydrogen bonding is of paramount importance in the bonding of cellulose fibers in paper is obscure, but probably dates almost to the origin of the concept of hydrogen bonding, which was in 1920.[28] Acceptance of hydrogen bonding has penetrated the paper industry erratically, but there now seems to be no detailed theory of fiber bonding which does not include recognition of the existence of hydrogen bonding between cellulose surfaces.

The essence of the hydrogen bond in cellulose is that adjacent hydroxyl groups have a strong attraction for each other, which may reach 5 kcal/mole. The hydrogen of the hydroxyl group, while not relinquishing its primary valence bond to the oxygen, also establishes a bridge with the oxygen of another hydroxyl group. Close proximity of the hydroxyl groups is required for hydrogen bonding to occur, approaching each other to within 2.5 to 3.5 Å, that is, within atomic distances.[29] Hydrogen bonds are formed by functional groups in which the hydrogen is attached to oxygen, most importantly, but alternatively to nitrogen or fluorine. The groups —OH and —NH$_2$ are important examples. Water is governed in its properties by hydrogen bonding. The ability of water to disintegrate paper is believed to be the results of its penetration into the web structure, followed by substitution of water-to-cellulose hydrogen bonds for cellulose-to-cellulose hydrogen bonds. The ability of water to swell cellulosic structures has the same explanation in hydrogen bonding.

The case of hydrogen bonding has been strongly presented by Nissan.[30,31] A key experiment[32] demonstrated the effect of various degrees of acetylation of beaten fibers of high-alpha eucalyptus pulp upon the tensile strength of papers made with them. As acetylation increased, the tensile strength of the papers decreased. Analysis of the data led to the conclusion that when the ability to form hydrogen bonds was lost, by acetylation of the hydroxyl groups of the cellulose composing the fibers, no other factors could compensate. That is, molecular character and organization, fibrillar and fiber strength, and all other factors had not been altered, but these were of no significance in contributing paper strength when the ability to form hydrogen bonds between the fibers was absent. In these experiments, nearly

40 percent of the stoichiometric number of hydroxyl groups per unit volume were chemically available for acetyl substitution. Of this 40 percent, however, only approximately one half were effective in forming interfiber bonds, showing that the other 80 percent must be sterically hindered from joining fibers or fibrils together. Stated differently, tensile strength was almost totally lost when the degree of substitution was 20 percent.

Broughton and Wang[33] adduced early evidence supporting the concept of hydrogen bonding. In one series of experiments, the tensile strength of seven commercial papers was measured while the papers were soaked in any of several liquids. The liquids were characterized by their energy-density coefficients, which are a measure of polarity. It was found that the tensile strength of the liquid-soaked paper decreased as the polarity increased, with water having the highest polarity and giving the lowest tensile strength. The results indicated that the fibers in the sheet are linked by secondary valence forces which can be broken by liquids in the order of the liquids' capability to form hydrogen bonds. No good correlation could be made between the tensile strength of the soaked paper and the surface tension of the liquid.[33]

In another series of experiments, hand sheets were formed in water, then either dried normally, dried by freezing and sublimation of the water, or dried by evaporation after first displacing the water with either an organic solvent or an aqueous solution of a surface-active agent. As before, tensile strength was measured, and expressed as energy-absorption capacity of the sheet. This series allowed the role of surface tension to be distinguished from the role of the polarity of the liquid in forming bonds. A mechanism of bond formation is indicated. When forming sheets in water in the usual way, the hydroxyl groups of the cellulose chains on the surface of the cellulose fibril are caused to be oriented toward the water, and hydrogen bonded to some of the water molecules. As drying progresses, the surface tension forces draw the fibrils together and some of the hydroxyl groups on adjacent fibrils may become close enough to hydrogen bridge with each other rather than with water molecules. As water is progressively withdrawn, this occurs more and more frequently, and finally the paper sheet, crosslinked by hydrogen bonds, is obtained. This process is interfered with if the fibrils are not brought close together (freeze drying or low surface tension), or if the orientation of the hydroxyl groups outwards toward the solution is lowered or suppressed (liquid of low polarity). Presence of a nonpolar liquid during sheet drying is more effective in prevention of bond formation than is wetting by the same liquid in destruction of bonds. While nonpolar liquids can inhibit formation of the bonds, unlike polar liquids, they cannot destroy them once formed. The bond-forming capacity appears to be more or less proportional to the energy density of the liquid, while the bond destruction power of a wetting liquid on paper increases in a more complex way with its energy density.[34]

Campbell[35] showed that, whereas a paper sample with a dry tensile strength of 7.28 kg was reduced to about 0.69 kg when wet with water, the tensile strength was reduced to only 2.32 kg when the paper was soaked with methyl alcohol. The tensile strength was higher than 2.32 kg when higher alcohols were used in place of methanol. Britt[36] describes similar experience.

Nissan[31] believes that hydrogen bonding not only holds fibers together but also holds the fibrils together within the fibers, the microfibrils within the fibrils, and crystallite bundles within the microfibrils. Ivanov[37] also reached the conclusion that the nature of the interfiber bonds in paper is the same as that of the intermolecular bonds in cellulose. However, where lignin is still present, masking the cellulose, as in groundwood, Ivanov concludes that bonding strength is due to cohesive forces (van der Waals').

From studies of the rheological behavior of paper and from supporting experiments, the fraction of hydrogen bonds which are actually involved in resisting tensile stress has been estimated. The total number of hydrogen bonds possible in a unit volume of the paper fiber network is equal to the number of hydroxyl groups in the cellulose, which can be calculated knowing the weight of cellulose in, and the density of, the paper. Corte et al[38] estimated that the interfiber bonds are hydrogen bridges originating from combination of about 0.5 to 2.0 percent of the hydroxyl groups. Nissan and Sternstein[30] agree, deriving further that the fraction will be related to the apparent density of the paper web, d: Fraction Bonded = $(d/1.6)^5$. For a very weak, unconsolidated paper with density of 0.3 gram/cm^3, Fraction Bonded = 0.00023 (0.023 percent). For a more conventional paper with density of 0.8 gram/cm^3, Fraction Bonded = 0.031 (3.1 percent). In an ingenious corroboration of these numbers, Corte, Kallmes, and Jarrot[39] contrived an apparatus which made the breaking of each hydrogen bond audible. The paper under stress was found to produce sounds and the number of "clicks" was in approximate agreement with the calculated number of broken hydrogen bonds.

Partial Solubility Theory

The similarity between the molecular interactions which promote bonding and those which cause substances to dissolve was observed long ago, and certain analogies are valid today. A hypothesis advanced by Urquhart[40] proposed that cellulose is soluble in water in certain stages. Campbell[41] extended the idea to beaten fibers, supposing that the cellulose crystallites on the surface of the fiber become partially "dissolved" in water and in this state attach themselves to similar crystallites on adjacent fibers. While in this state of near solution, the molecules or crystallites are endowed with a certain freedom of movement and can arrange themselves so that they are pulled together when water is removed. Clark[42] suggested that the surface of well-beaten fibers is a "two-dimensional colloidal system," in which the surface fibrillae have two dimensions in the colloidal range, but are anchored to the fiber in the third dimension. Thus, these fibrillae, which are made up of units as least as thick as cellulose crystallites, act almost as if they were in colloidal solution. The degree of adhesiveness between fibrillae depends on the degree of colloidal solubility, which is presumably inversely proportional to the degree of polymerization of the cellulosic and hemicellulosic material making up the fibrillae. Possibly the degree of crystallinity is a better criterion than the degree of polymerization.

The idea of a partial solubility as an essential part of bonding has been extended and made very general. Over a period of years, Voyutskii has developed a comprehensive theory which has received formidable experimental support, and which is

known as the diffusion theory of polymer adhesion.[43] Voyutskii was addressing himself to the adhesion of synthetic polymers and did not consider cellulose particularly. A portion of the theory states that adhesion can occur only when segments of macromolecular chains of one component can diffuse across the interface into the surface layers of the other component. There is in effect a "solution" of one polymer surface into the other polymer surface as a result of this diffusion. Solvents may play an important part in promoting the diffusion, analogous to the critical effect of water in cellulose-to-cellulose adhesion or bonding. McKenzie[44] has examined the bonding of cellulosic fibers in the light of the Voyutskii theory. He regards it as an extension of present theories of fiber bonding. The diffusion is aided by the microfibrillar nature of the fiber wall. Areas of interfiber contact are established under the controlling influence of conformability, followed by movement of molecular segments across the interface, and fixation of such segments by hydrogen bonds as water is removed from the system. The emphasis by Clark[45] upon the fundamental importance to bonding of near-molecular-size fibrillar fuzz on the surfaces of fibers is consistent with the diffusion hypothesis.

The partial solubility theory and the diffusion theory help us to understand the means by which molecules on fiber surfaces come into sufficiently close contact for bonding to occur. Neither idea is restricted to acqueous systems. Thus, while cellulose fibers will not form a strong sheet of paper in acetone or nonpolar liquids, fibers of cellulose acetate or cellulose ether, which are partially soluble in acetone, will form exceptionally strong sheets in this medium.[46] Cellulose acetate will also form strong sheets in alcohol, since the fibers are partially soluble in this liquid as well. However, neither of these highly substituted cellulose derivatives will produce strong paper when water is used as the dispersing medium because the fibers are not hydrated by the water.

In any case, the action of the fiber surface with the solvent is a precursor to the bonding of the fiber surfaces with each other. After the fiber surfaces have come into intimate contact through "partial solubility" of the surface in a solvent, and by diffusion of segments of the macromolecular chains in the surface, the subsequent bonding will depend upon the chemistry of the macromolecules. With cellulose fibers, the bonding is primarily between hydroxyl groups on adjacent chains, and is by hydrogen bonding. With cellulose acetate, the opportunity for hydrogen bonding is small, but the strength of cellulose acetate papers shows the presence of other bonds, either the polar or the van der Waal type.

Nature of Fiber Surface

The preceding theories lead to the conclusion that the ability of cellulose fibers to produce fiber-to-fiber bonding is dependent upon the hydrophilic nature of the fiber surface, and the consequent ability to form hydrogen bonds. The presence of hemicellulosic material is favorable to fiber bonding in that it improves the contact of adjacent hydroxyl-containing surfaces. It is informative to consider the effect of interferences with the hydroxyl-rich surfaces of the cellulosic fibers, either as the result of adsorbed substances or as the result of chemical modification.

Dixson[47] has shown that the adsorption of hydrophobic materials or surface-active agents on the surface of cellulose fibers greatly decreases the amount of fiber-to-fiber bonding, probably because these agents are adsorbed on the fiber surface in such a way that the large hydrophobic group protrudes from the surface of the fiber and reduces the hydrophilic nature of the fiber surface. It is common practice in mills desiring to soften their papers to add long-chain amines to the furnish. The resulting "softness" is due to decreased fiber-to-fiber bonding. The sheet-forming qualities of pulps are also reduced by treatment with tannic acid, probably because of the interference with the hydrophilic character of the fiber surface. Britt[36] reported that the tensile strength of filter paper was much reduced when the paper was dipped in a water solution of cetyldimethylbenzyl ammonium chloride and then dried, but the tensile strength was unaffected when the paper was dipped in a water solution of Congo Red and dried. He believed that the cationic material was adsorbed on the outside surface of the fibers, thus interfering with bonding, while the dye entered the interstices of the cell wall and was ad-sorbed there, thus leaving the outer bonding surfaces of the fiber unaffected. Bruun and coworkers[48] found that addition of surfactants to the furnish before hand sheets were made lowered the burst and tensile strengths, whether the surfactants were anionic, cationic, or nonionic, and whether the pulps were unbleached or bleached sulfite, or bleached kraft. The tearing strength and opacity did not always increase correspondingly to the decrease in burst and tensile strengths. They thought that the results were more influenced by the nature of the pulp than by the nature of the surface-active agent.

A number of workers have studied the effect of partial replacement of the hy-droxyl groups on cellulose fibers. In general, when the substituent is hydrophobic, the water affinity of the fibers is reduced and the strength of the paper made from them is reduced. An exception to this generality is observed when the degree of substitution is low. Apparently the introduction of a few substituent groups, even though they are hydrophobic, somehow opens the fiber structure, and actually makes a greater number of hydroxyl groups accessible for hydration and partial solubilization than were accessible in the original fiber. This initial increase in inter-fiber bonding capacity has been observed as the result of acetylation and priopionyl-ation[46,49,50] or of methoxylation.[49] The increase in paper strength with low degree of substitution is more marked with cotton rag fiber or with long-fibered bleached kraft pulps than for short-fibered eucalyptus alpha cellulose.[50] Nissan and Stern-stein[36] made use of the loss of bonding from the acetylation of moderately beaten high-alpha cellulose eucalyptus pulp to support the hydrogen-bond theory of cel-lulosic fiber bonding, since this pulp does not show the increase of bonding due to a low degree of substitution with acetyl groups. Higgins, McKenzie, and Harrington[50] found that as the degree of beating is increased in a long-fibered bleached kraft pulp, the initial increase in tensile strength and rupture energy with degree of acetylation is less, and suggest that the initial rise in the bonding capacity of the unbeaten fibers with increasing degree of substitution is, in part, a simulation of the beating process. Actual beating eventually overtakes the chemically induced strength increase, but the two effects are not additive. If the group substituted for the hy-

droxyl group on cellulose is as hydrophilic as the hydroxyl group, the water affinity of the fibers and the strength of the paper made from them is not impaired. Walecka,[51] using carboxymethylated beaten cotton rag pulp, found that the affinity of the fibers for water was increased and that papers made from the carboxymethylated fibers were stronger than the original. Walecka deliberately limited the degree of substitution to a level that would not destroy the integrity of the fibers, nor make them completely soluble, substituting about 6 percent or less of the hydroxyl groups with carboxymethyl cellulose. The carboxymethylation did not occur uniformly through the fibers since there was some dissolving of the fibers even at the lowest degrees of substitution. Talwar[52] found that strength improvement resulted only with sodium salt of the carboxymethyl cellulose fibers. When alum or acid was added, hydrophilic character was decreased and the strength improvement was lost.

The process of chemical pulping introduces hydrophilic groups into the cellulose, especially carboxylic groups; sulfonic acid groups are introduced in the case of sulfite pulping. The influence of such acidic groups on the properties of unbleached high-yield pulps has been studied by Eriksson and Sjostrom. The effect may be studied either by adding more acidic groups of the same kind or by blocking those present by esterification. When the blocking was done by esterification with propylene oxide, under conditions believed to cause no other changes, the resulting paper properties indicated that the acidic groups had been contributing to interfiber bonding and that the esterification eliminated their contribution to bonding. Comparisons were made between esterification before and after refining. Paper properties were compared on an equal freeness basis and also by plotting bulk against tensile strength (breaking length). On either an equal-freeness basis or an equal-bulk basis, the esterified pulps produced papers that were lower in strength. The magnitude of the difference decreased as the amount of refining increased. Esterifying the refined pulp always raised the freeness and decreased the water-retention value.[53]

The discussion above indicates that the chemical nature of the fiber surface is of great importance to bonding, particularly if the hydroxyl groups are modified either by adsorbed substances or by chemical substitution of groups of greater or less hydrophilic character. The subject of the deliberate chemical modification of cellulosic fibers for paper making is a large one. For example, papers are modified by acetylation or cyanoethylation to improve their insulating properties. Efforts have been made to preserve the essential strength properties of kraft papers by chemical modification and at the same time impart resistance to degradation caused by aging and heat.[54]

Measurement of Fiber Bonding and Strength of Bonds

The most important factors involved in fiber bonding are the area of the fibers in contact, the number of bonds within the area of contact, and the strength of each bond. Conventional methods of testing the strength of paper do not characterize the bonds themselves, much less distinguish the above factors, although beating and other treatments which increase the tensile and bursting strength are said to